GW density matrix with ABINIT

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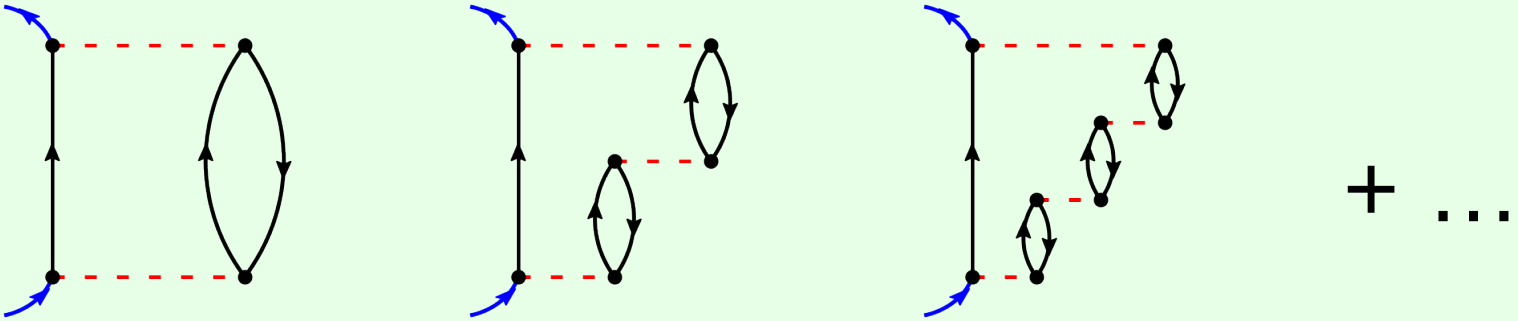
What is *GW*?

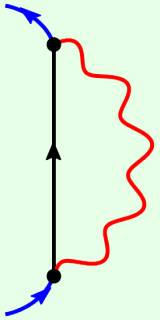
Infinite summation of diagrams over one single class: the rings

GW



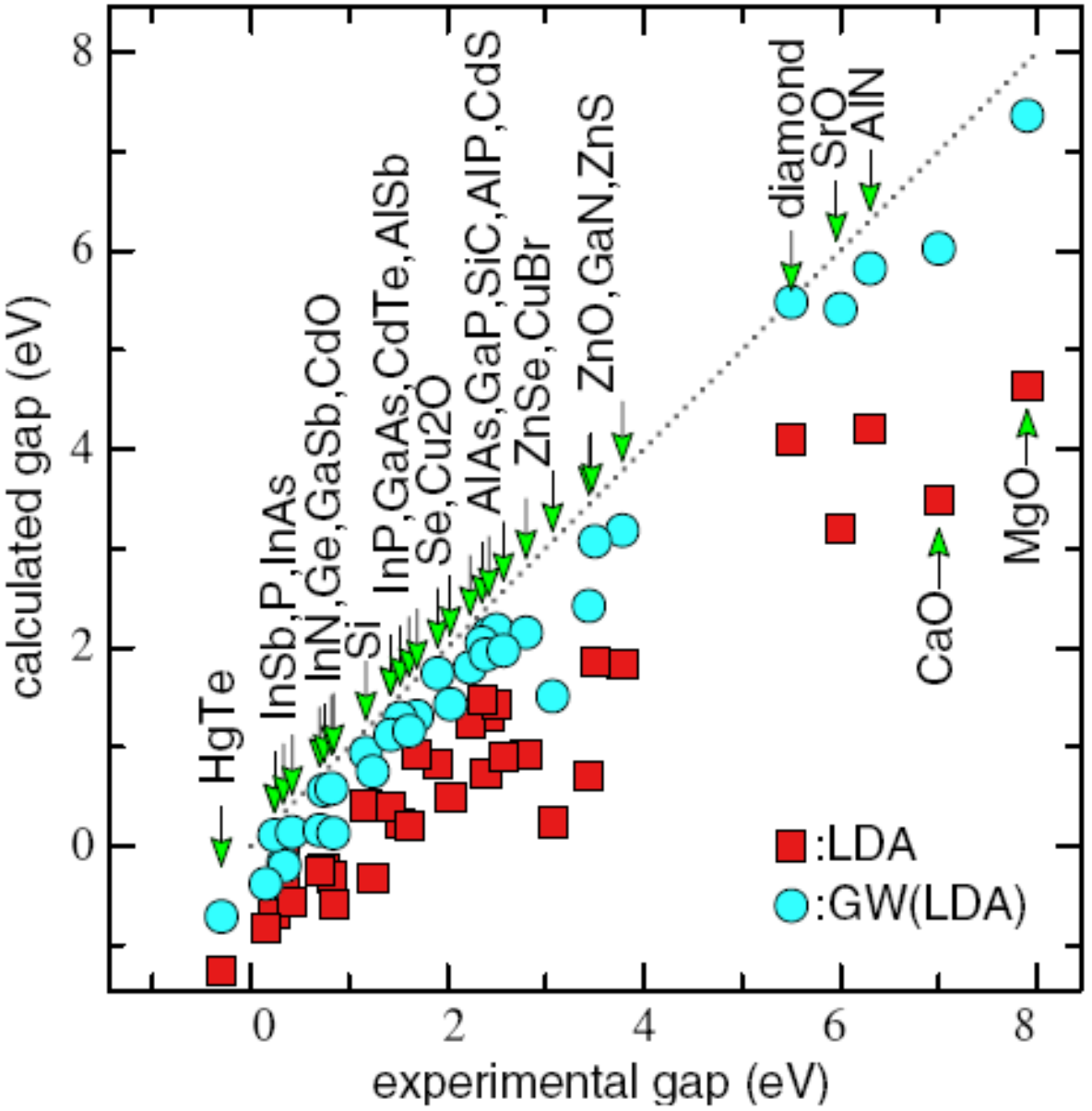
1-ring 2-rings 3-rings + ... *n*-rings

=



RPA for the screened Coulomb interaction

What is *GW*?


calculated gap (eV)
experimental gap (eV)
0
2
4
6
8
HgTe
InSb,P,InAs
InN,Ge,GaSb,CdO
Si
InP,GaAs,CdTe,AlSb
Se,Cu2O
AlAs,GaP,SiC,AlP,CdS
ZnSe,CuBr
ZnO,GaN,ZnS
diamond
SrO
AlN
CaO
MgO
:LDA
:GW(LDA)

Outline

1) A finalized contribution to ABINIT:

   Coulombic divergence integration in the exchange operator

2) A contribution to come:

   Linearized *GW* density matrix for solids

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Reproducibility in G_0W_0

Cross validation among PW codes: ABINIT, BerkeleyGW, Yambo

Translation: Why do we still get different results with different codes?

Reproducibility in G_0W_0 Calculations for Solids

Tonatiuh Rangel,[1,2,*] Mauro Del Ben,[3] Daniele Varsano,[4,5] Gabriel Antonius,[2,6,7] Fabien Bruneval,[8,1,6] Felipe H. da Jornada,[2,6] Michiel J. van Setten,[9,5,10] Okan K. Orhan,[11] David D. O'Regan,[11] Andrew Canning,[3] Andrea Ferretti,[4,5] Andrea Marini,[12,5] Gian-Marco Rignanese,[9,5] Jack Deslippe,[13] Steven G. Louie,[2,6] and Jeffrey B. Neaton[1,2,14,†]

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Ab initio many-body perturbation theory within the *GW* approximation is a Green's function formalism widely used in the calculation of quasiparticle excitation energies of solids. In what has become an increasingly standard approach, Kohn-Sham eigenenergies, generated from a DFT calculation with a strategically-chosen exchange correlation functional "starting point", are used to construct G and W, and then perturbatively corrected by the resultant *GW* self-energy. In practice, there are several ways to construct the *GW* self-energy, and these can lead to variations in predicted quasiparticle energies. For example, for ZnO and TiO_2, reported *GW* fundamental gaps can vary by more than 1 eV. In this work, we address the convergence and key approximations in contemporary G_0W_0 calculations, including frequency-integration schemes and the treatment of the Coulomb divergence in the exact-exchange term. We study several systems, and compare three different *GW* codes: BerkeleyGW, Abinit and Yambo. We demonstrate, for the first time, that the same quasiparticle energies for systems in the condensed phase can be obtained with different codes, and we provide a comprehensive assessment of implementations of the *GW* approximation.

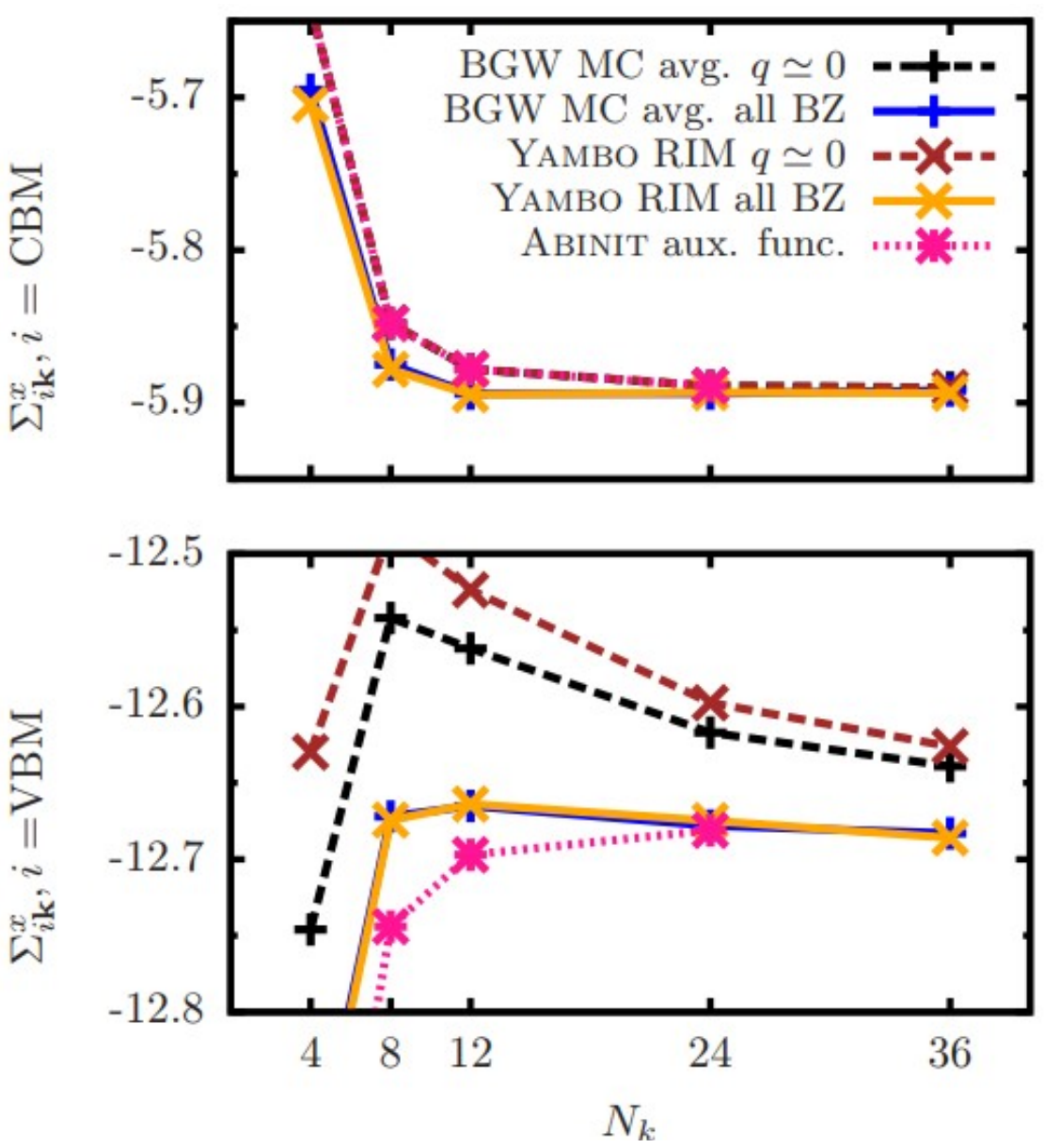
F. Bruneval, *GW* density matrix

Abidev, 2019

Exchange operator converges slowly

Bulk silicon

convergence
wrt **k**-points



1. ABINIT: the worst of all codes
2. exchange operator: also present in hybrid functionals

Exchange operator within PW

Exact exchange in PW:

Coulomb interaction

Density matrix

$$\langle i\mathbf{k}|\Sigma_x|j\mathbf{k}\rangle = -\sum_{\mathbf{q},\mathbf{G}} v(\mathbf{q}+\mathbf{G}) \sum_{v\in occ.} M_{iv\mathbf{k}}(\mathbf{q}+\mathbf{G}) M^*_{jv\mathbf{k}}(\mathbf{q}+\mathbf{G})$$

where the matrix elements are

$$M_{iv\mathbf{k}} = \langle i\mathbf{k}|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|v\mathbf{k}-\mathbf{q}\rangle$$

and the Coulomb interaction is

$$v(\mathbf{q}+\mathbf{G}) = \frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2}$$

Exchange operator within PW

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where the matrix elements are

$$M_{iv\mathbf{k}} = \langle i\mathbf{k}|e^{i(\mathbf{q}+\mathbf{G})\cdot\mathbf{r}}|v\mathbf{k}-\mathbf{q}\rangle$$

Behavior at **q** = **G** = 0

$$\rightarrow \quad \delta_{i\,v}$$

and the Coulomb interaction is

$$v\left(\mathbf{q}+\mathbf{G}\right)=\frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2}$$

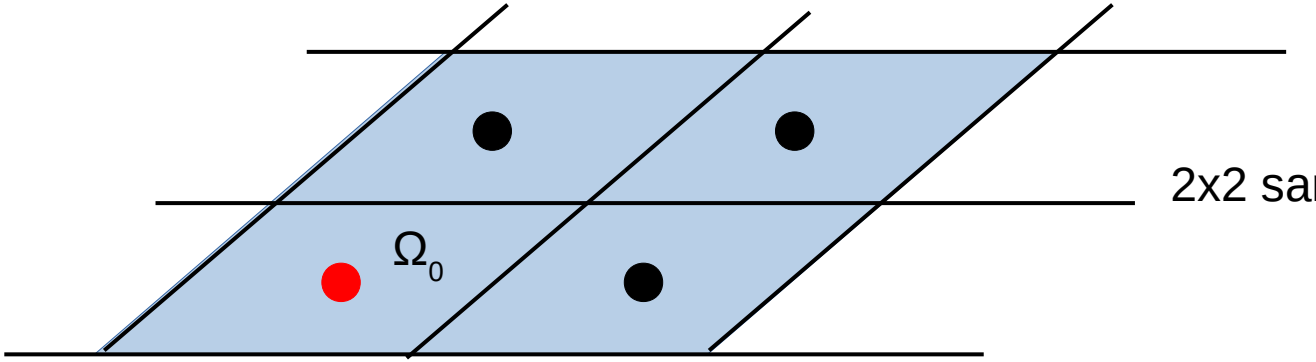
Integrable divergence in 3D

$$\rightarrow \quad \propto \int_0^{q_c} dq\, 4\pi q^2 \frac{1}{q^2}$$

Monte Carlo sampling of the miniBZ

Purpose: integrate the Coulomb interaction at **q**=0
in the arbitrary shape volume of the BZ around **q**=0, Ω_0

$$\int_{\Omega_0} d\,\mathbf{q}\, v(\mathbf{q}) = \frac{\Omega_0}{N_{\mathrm{MC}}} \sum_{\mathbf{q}\in\Omega_0} \frac{4\pi}{q^2}$$



2x2 sampled Brillouin zone

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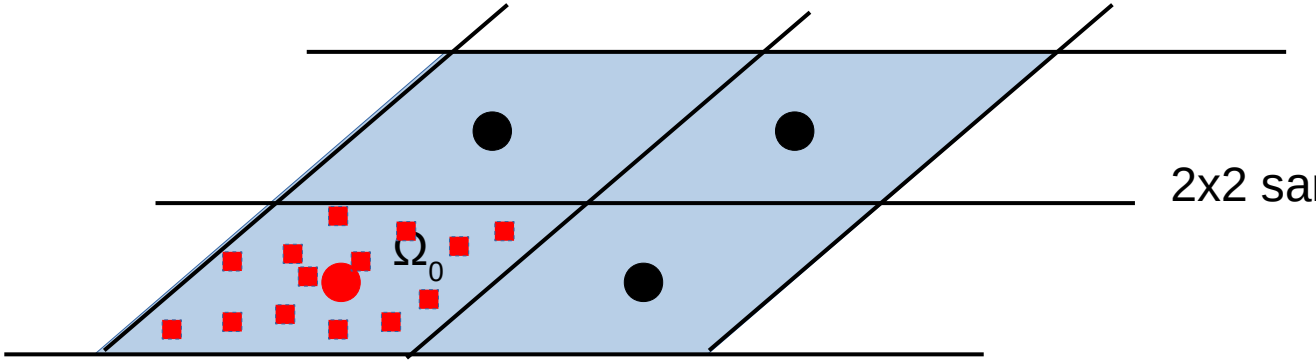


2x2 sampled Brillouin zone

Two parameters:

`icutcoul 14, 15, 16` for short-, long-, any-range exchange

And N_{MC} hard-coded to 2,500,000

Outline

1) A finalized contribution to ABINIT:

Coulombic divergence integration in the exchange operator

2) A contribution to come:

Linearized *GW* density matrix for solids

Density matrix

Obtained from a Green's function or from a mean-field approx.

$$\gamma(\boldsymbol{r},\boldsymbol{r}') = -i\,G(\boldsymbol{r}\,t,\boldsymbol{r}'\,t^{+}) \qquad \gamma(\boldsymbol{r},\boldsymbol{r}') = \sum_i f_i\,\varphi_i(\boldsymbol{r})\,\varphi_i^{*}(\boldsymbol{r}')$$

Electronic density

$$\gamma(\boldsymbol{r},\boldsymbol{r}) = n(\boldsymbol{r})$$

Kinetic energy

$$\langle T \rangle = -\frac{1}{2}\int d\boldsymbol{r}\,\lim_{\boldsymbol{r}'\to\boldsymbol{r}}\nabla^2_{\boldsymbol{r}'}\,\gamma(\boldsymbol{r},\boldsymbol{r}')$$

Hartree energy

$$\langle E_H \rangle = \frac{1}{2}\int d\boldsymbol{r}\,d\boldsymbol{r}'\,\gamma(\boldsymbol{r},\boldsymbol{r})\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\gamma(\boldsymbol{r}',\boldsymbol{r}')$$

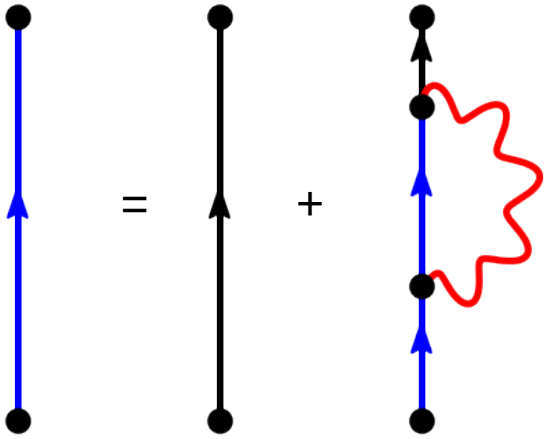
Exchange energy

$$\langle E_x \rangle = -\frac{1}{2}\int d\boldsymbol{r}\,d\boldsymbol{r}'\,\gamma^{*}(\boldsymbol{r},\boldsymbol{r}')\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\gamma(\boldsymbol{r}',\boldsymbol{r})$$

In summary: Everything but the electronic correlation energy

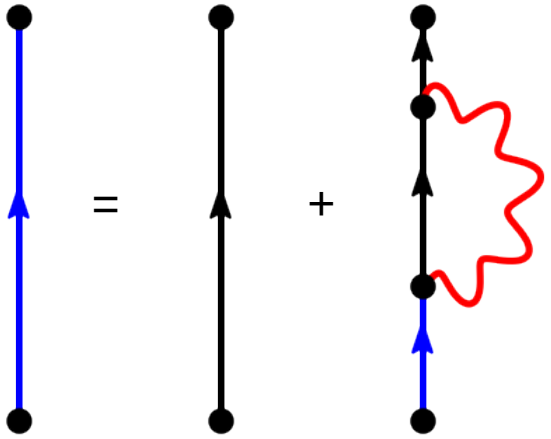
Linearized Dyson equation

Dyson equation

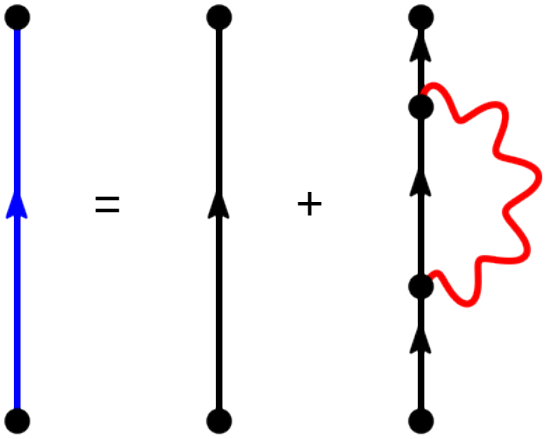


$$G = G_0 + G_0 \Sigma G$$

One-shot *GW*

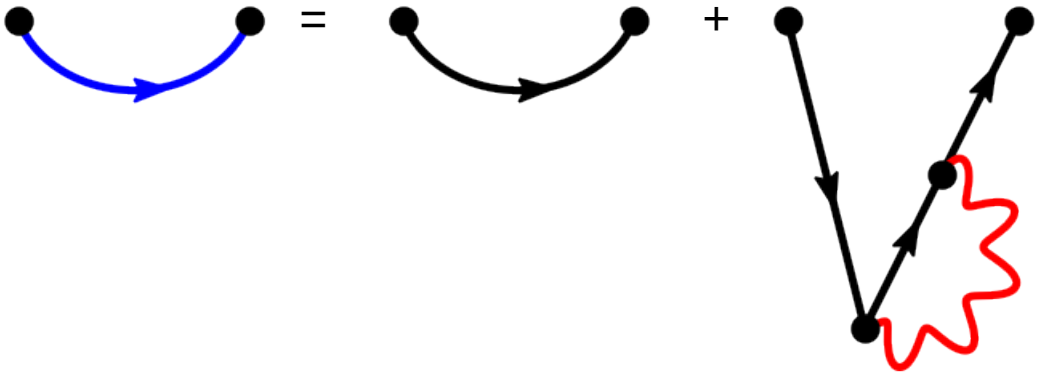


Linearized Dyson

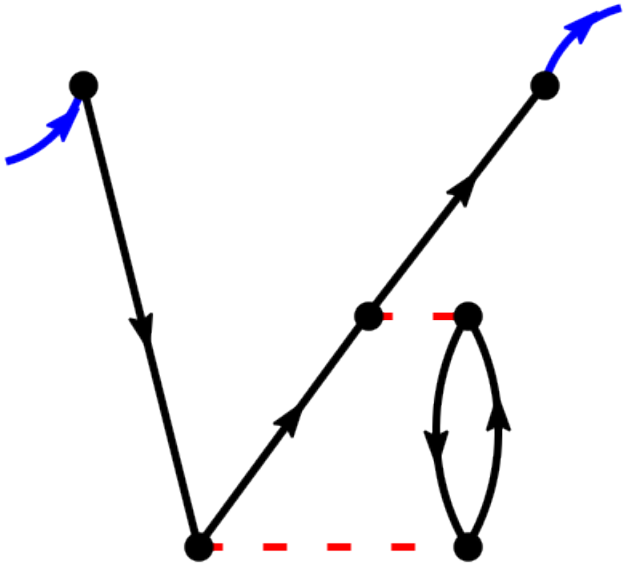


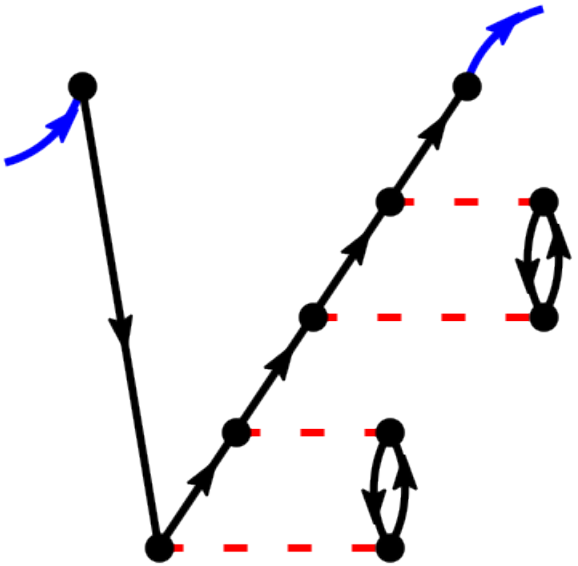
time

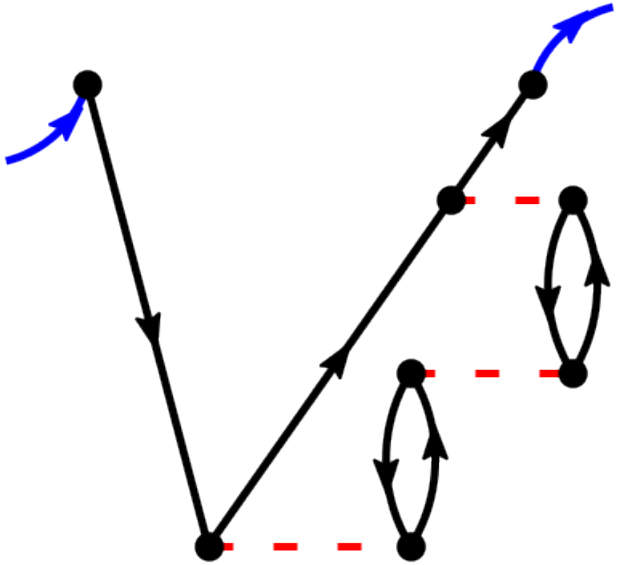
Equal time Green's function = density matrix $\gamma(\boldsymbol{r},\boldsymbol{r}') = -i\,G(\boldsymbol{r}\,t,\boldsymbol{r}'\,t^{+})$

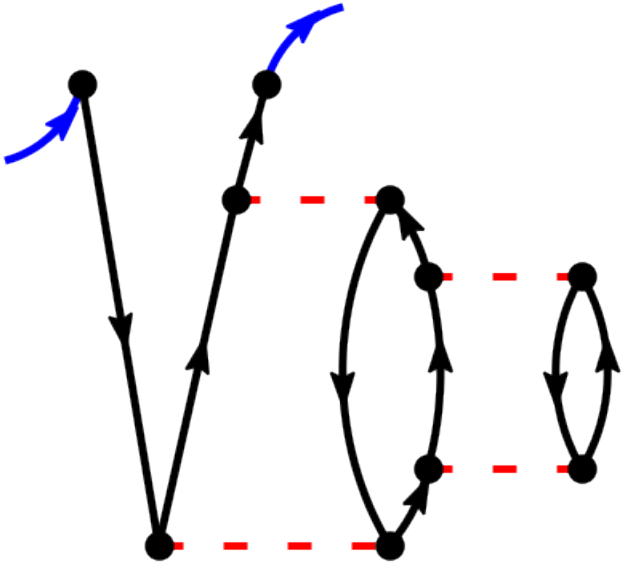


“Linearized” GW density matrix









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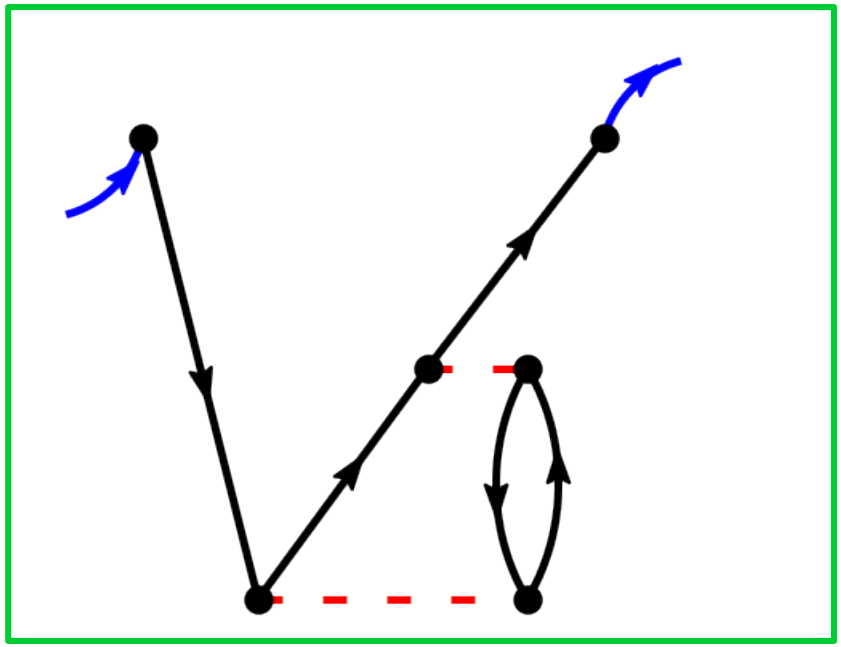
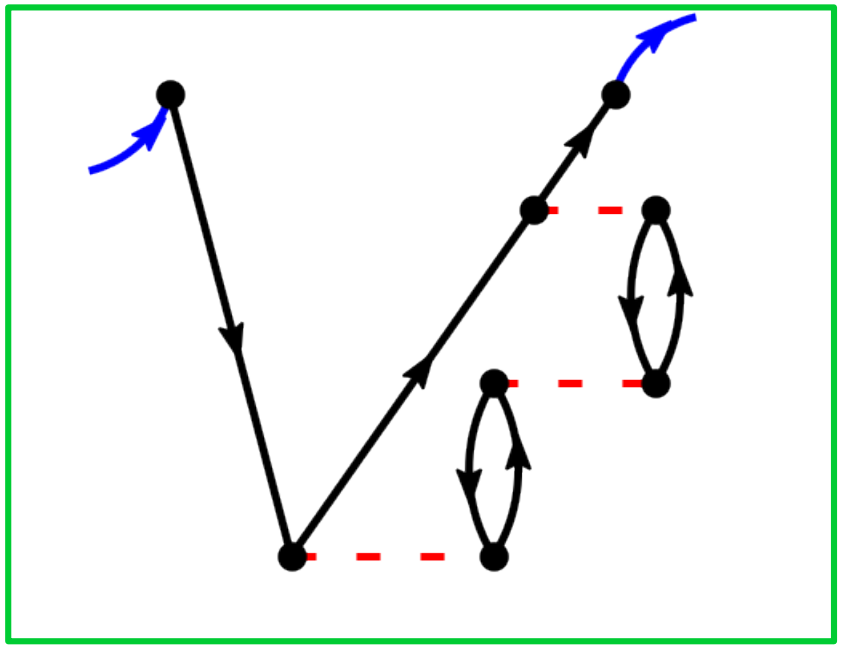
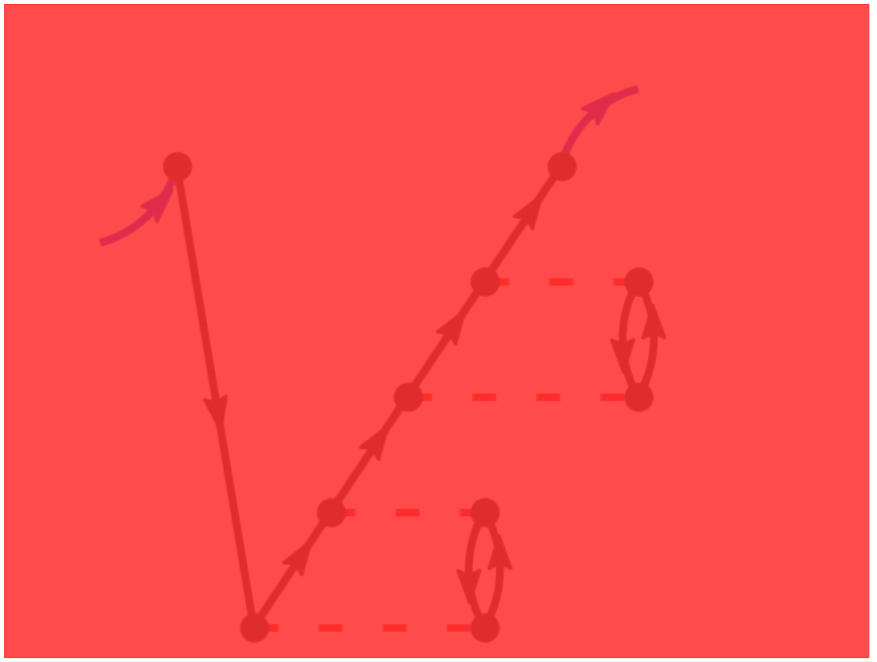
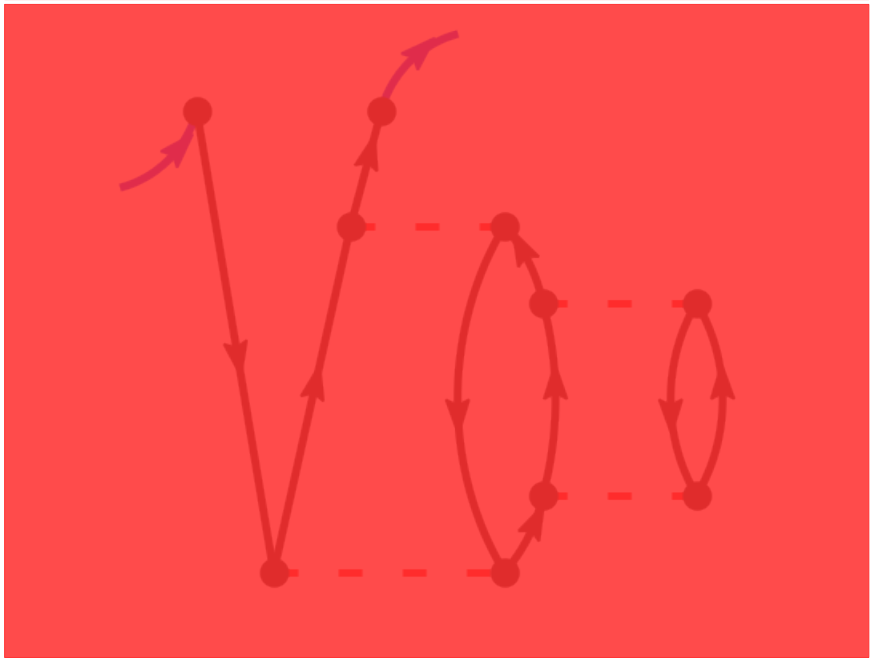


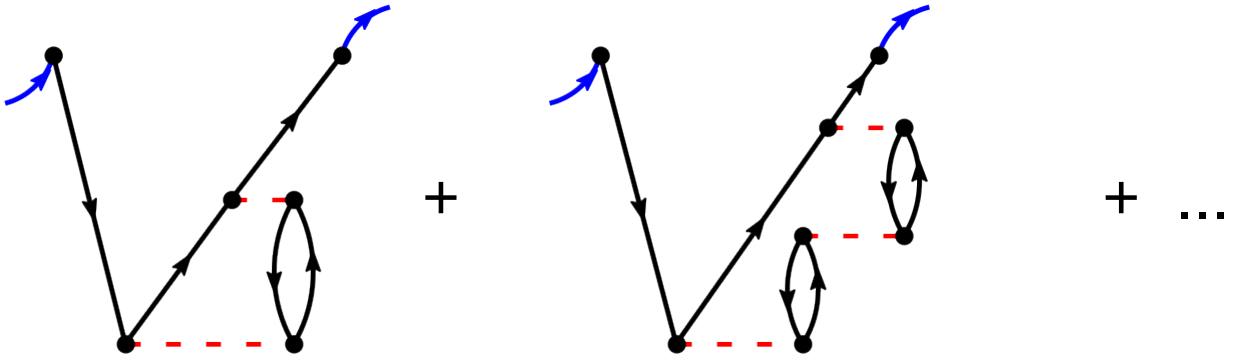






“Linearized” *GW* density matrix

or how to simulate self-consistent *GW* without doing it



Simple formula:

occ-occ

$$D_{ij}^{GW} = 2\delta_{ij} - 2\sum_{sa} \frac{w_{ia}^s}{\epsilon_i - \epsilon_a - \Omega_s} \frac{w_{ja}^s}{\epsilon_j - \epsilon_a - \Omega_s}$$

virt-virt

$$D_{ab}^{GW} = 2\sum_{si} \frac{w_{ia}^s}{\epsilon_i - \epsilon_a - \Omega_s} \frac{w_{ib}^s}{\epsilon_i - \epsilon_b - \Omega_s}$$

occ-virt

$$D_{ib}^{GW} = -\frac{2}{\epsilon_i - \epsilon_b} \sum_{sj} \frac{w_{bj}^s w_{ij}^s}{\epsilon_j - \epsilon_b - \Omega_s} + \frac{2}{\epsilon_i - \epsilon_b} \sum_{sa} \frac{w_{ia}^s w_{ba}^s}{\epsilon_i - \epsilon_a - \Omega_s},$$

MOLGW

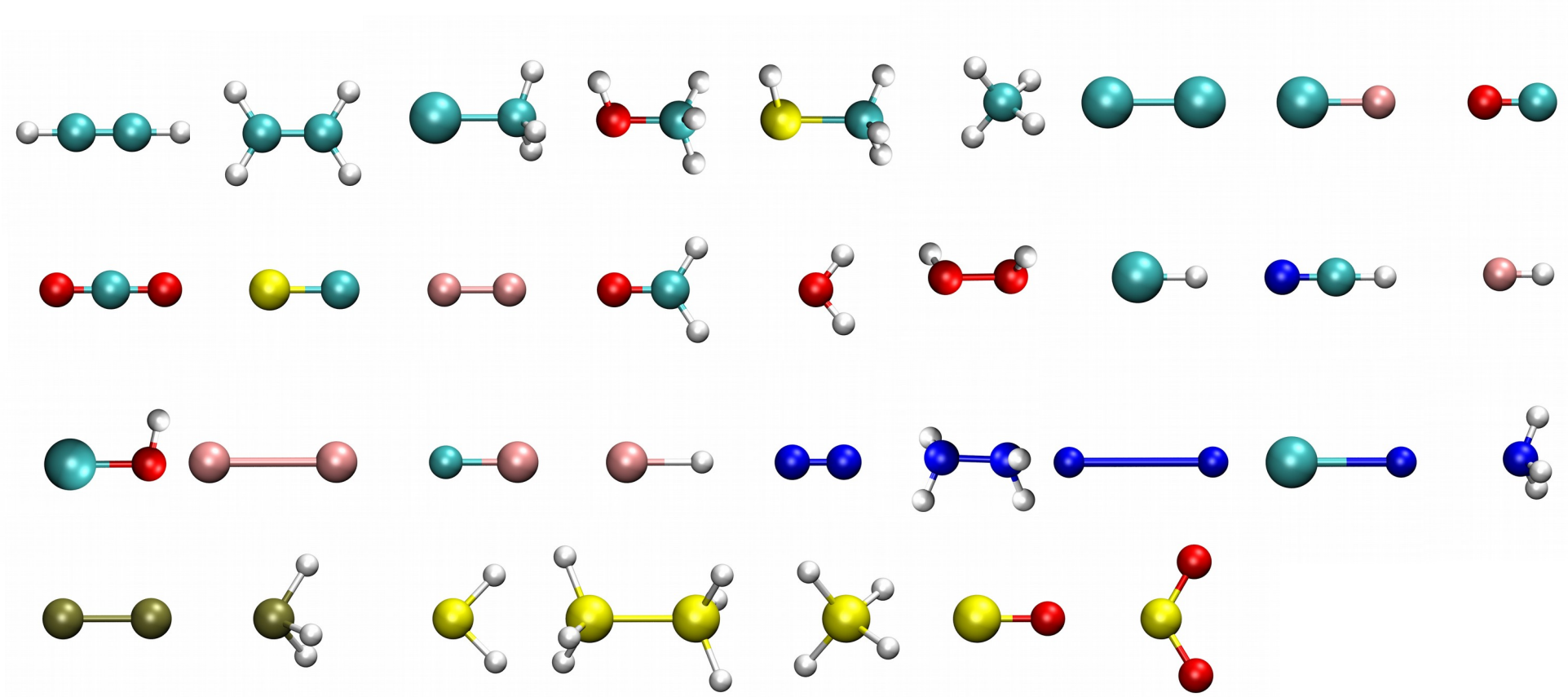
Comparison to sc*GW* dipoles

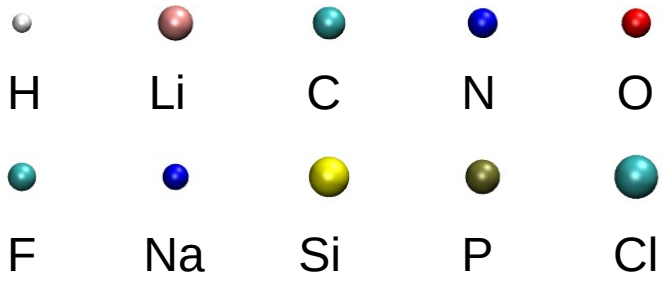
	LiH	HF	LiF	CO
scGW bond length [29]	1.579	0.919	1.586	1.118
scGW [29]	5.90	1.85	6.48	0.07
D^{GW}	5.91	1.84	6.42	0.10
D^{PT2}	5.90	1.80	6.33	0.41
HF	5.96	1.93	6.52	-0.22
CCSD	5.92	1.85	6.37	0.10

[29] Caruso, Rinke, Ren, Rubio, Scheffler, Phys. Rev. B (2013)

Bruneval, Phys. Rev. B (2019)

34 molecules benchmark: ionization potential





Reference density matrix within CCSD

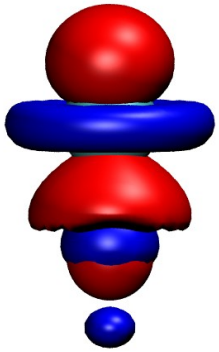
$$D^{\mathrm{CCSD}}$$

in a good basis set “cc-pVQZ”

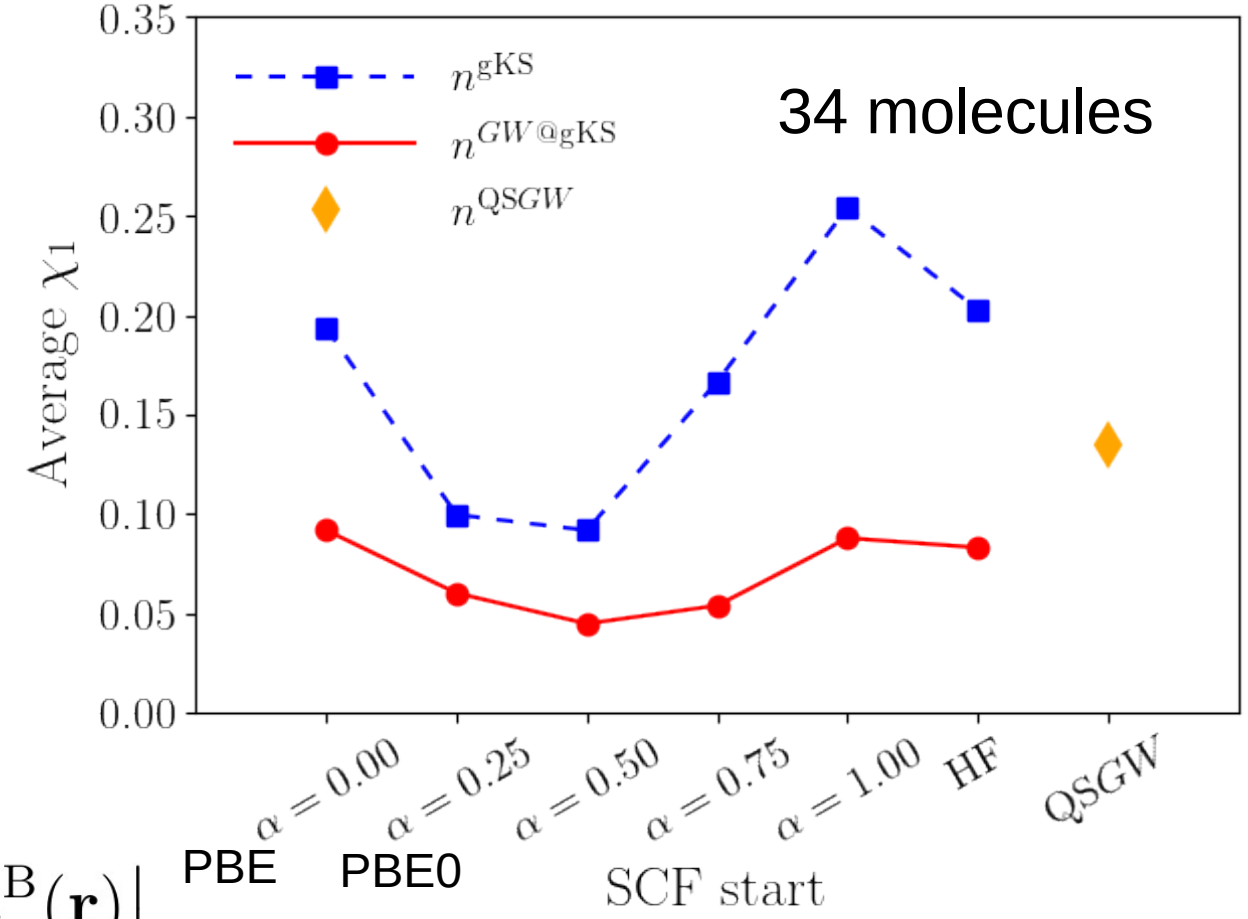
F. Bruneval & MAL Marques, JCTC (2013)

Density quality

CO



GW - CCSD

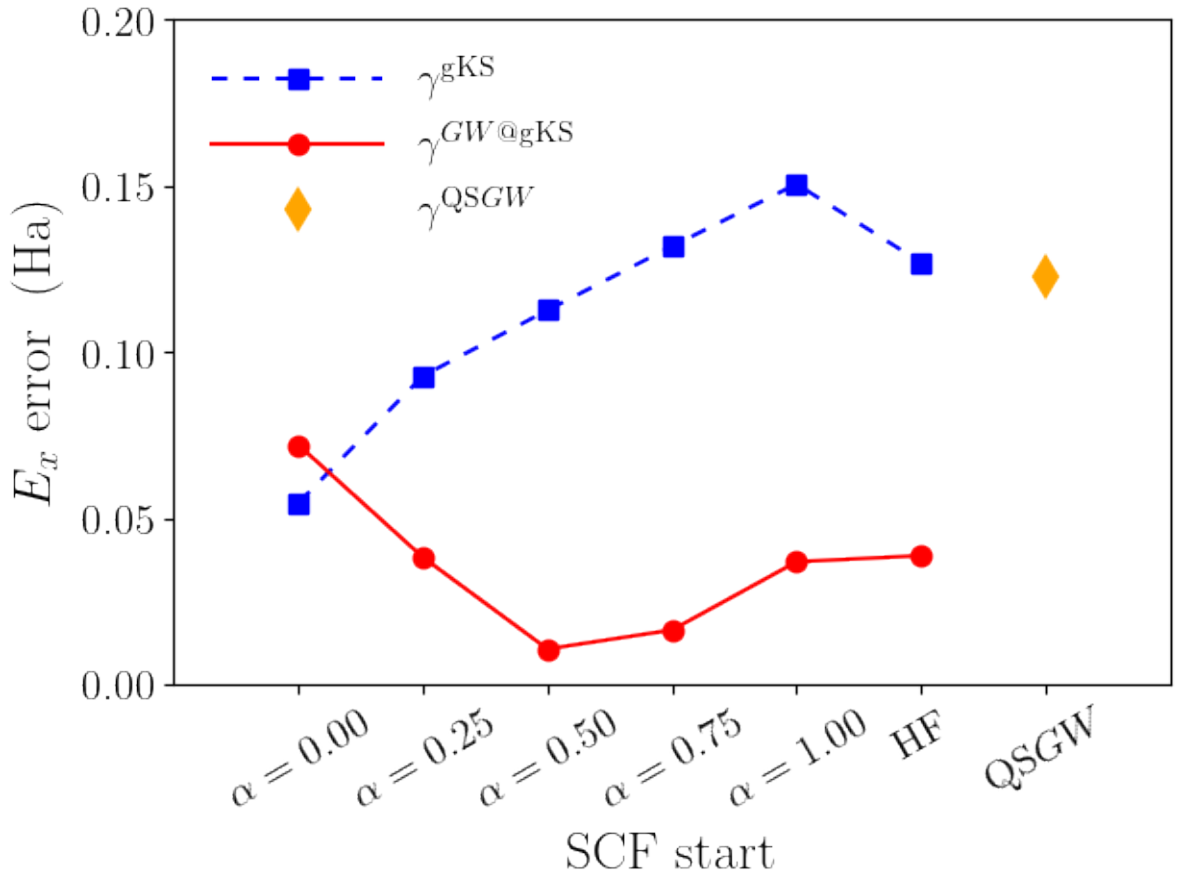


$$\chi_1^{\mathrm{AB}} = \int d\mathbf{r} \left| n^{\mathrm{A}}(\mathbf{r}) - n^{\mathrm{B}}(\mathbf{r}) \right|$$

QS*GW*: $$\Sigma^{\mathrm{QSGW}}_{c pq\sigma} = \frac{1}{4}[\Sigma^{\sigma}_{c pq}(\epsilon_{p\sigma}) + \Sigma^{\sigma}_{c qp}(\epsilon_{p\sigma}) + \Sigma^{\sigma}_{c pq}(\epsilon_{q\sigma}) + \Sigma^{\sigma}_{c qp}(\epsilon_{q\sigma})]$$

Density matrix quality

$$\langle E_x \rangle = -\frac{1}{2} \int d\boldsymbol{r}\, d\boldsymbol{r}'\, \gamma^*(\boldsymbol{r},\boldsymbol{r}') \frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|} \gamma(\boldsymbol{r}',\boldsymbol{r})$$



Density matrix in imaginary frequencies

$$G = G_0 + G_0 \Sigma_c G_0$$

$$D_{\boldsymbol{k}pq} = D^{\mathrm{HF}}_{\boldsymbol{k}pq} - \frac{\mathrm{i}}{2\pi} \int_{-\infty}^{\infty} d\,\omega \frac{1}{\mathrm{i}\,\omega - \epsilon_{\boldsymbol{k}p}} \langle p\boldsymbol{k}|\Sigma_c(\mathrm{i}\,\omega)|q\boldsymbol{k}\rangle \frac{1}{\mathrm{i}\,\omega - \epsilon_{\boldsymbol{k}q}}$$

Marc T.

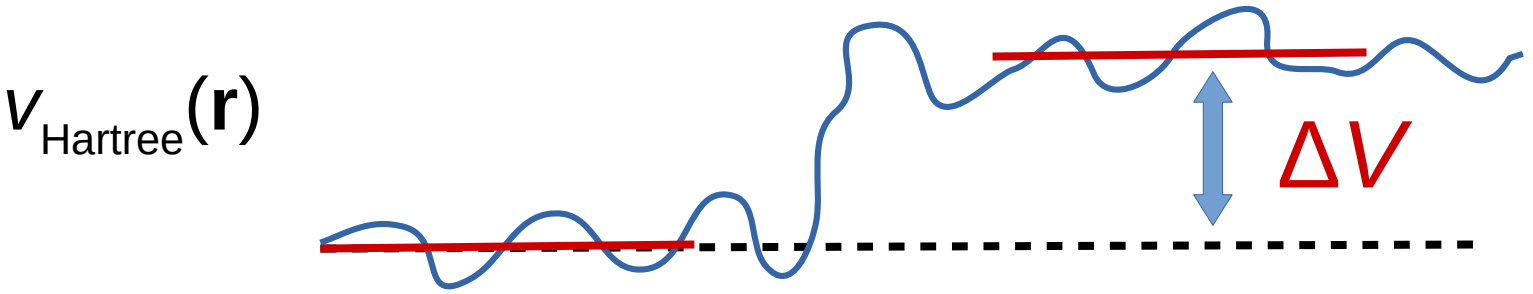
Fabien B.

$\gamma(\boldsymbol{r}, \boldsymbol{r}'), n(\boldsymbol{r})$

Already in Abinit for $p = q$

Having improved densities in solids

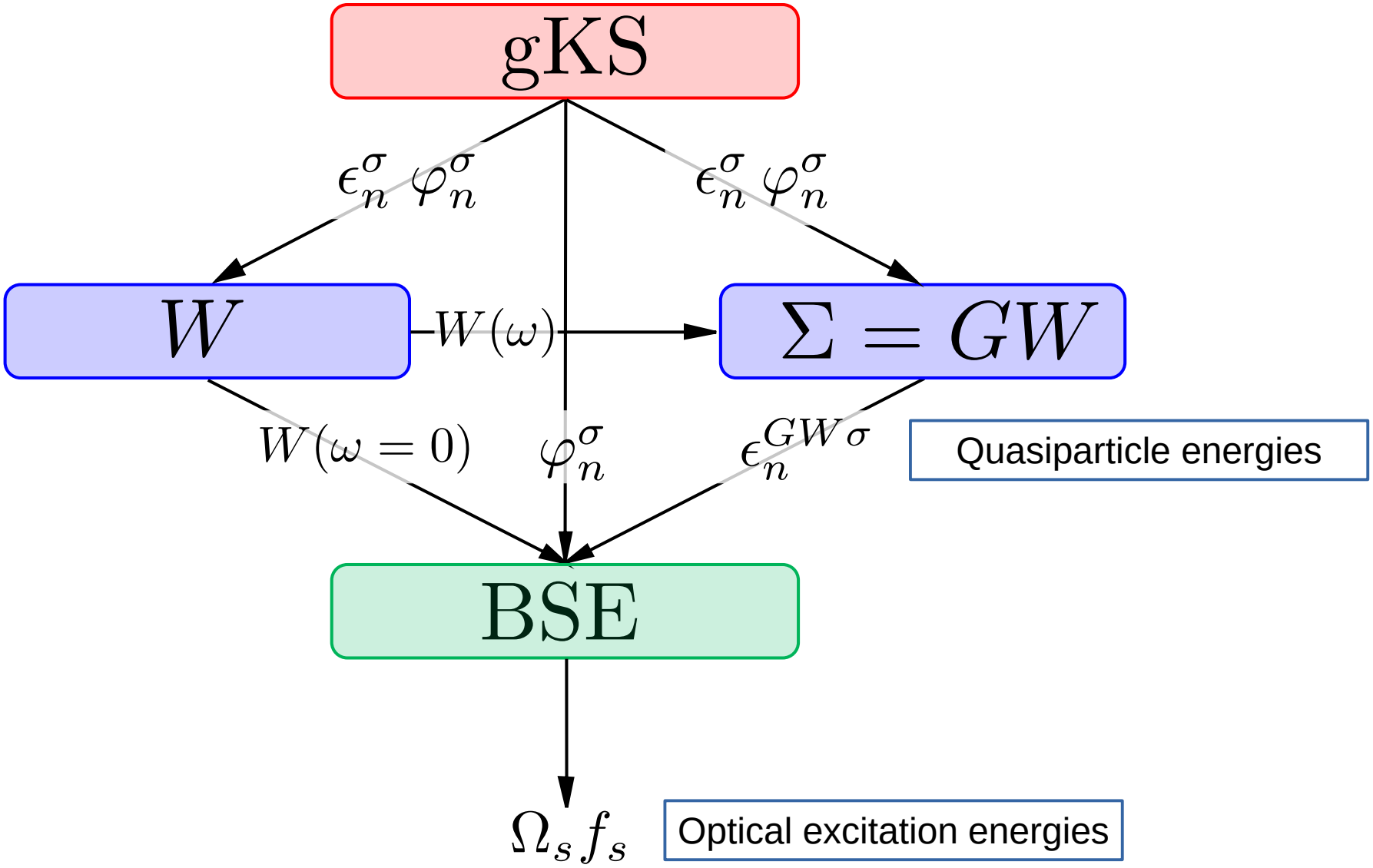
Revisit the band offsets “à la Shaltaf-Rignanese-Pasquarello” PRL 2008



Supplemental information

GW / BSE work flow: the “one-shot” procedure

Also named $G_0 W_0$



MOLGW: recycling old quant. chem. recipes

Ingredients:

- Real Gaussian basis functions:

$$\phi_\mu(\boldsymbol{r}) = Y_{lm}(\hat{\boldsymbol{r}})\, r^l \sum_i c_i e^{-\alpha_i r^2}$$

=> from Basis Set Exchange website

https://bse.pnl.gov/bse/portal

- Wavefunctions (LCAO):

$$\varphi_i(\boldsymbol{r}) = \sum_\mu C_{\mu i}\, \phi_\mu(\boldsymbol{r})$$

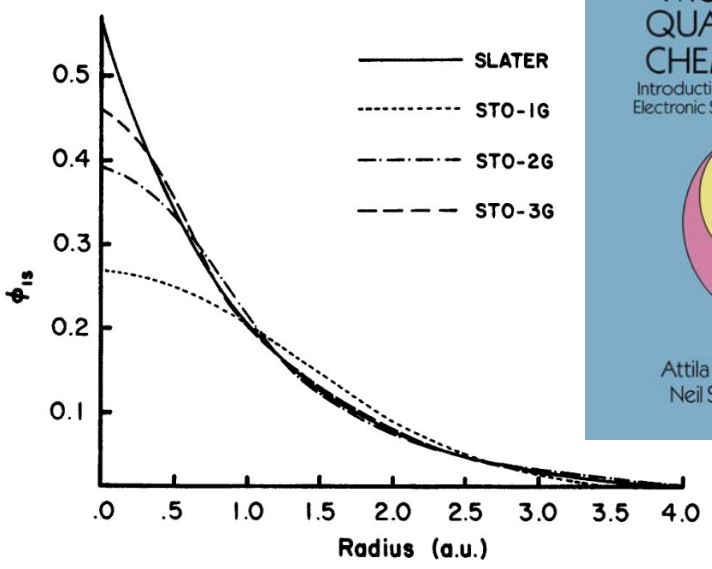
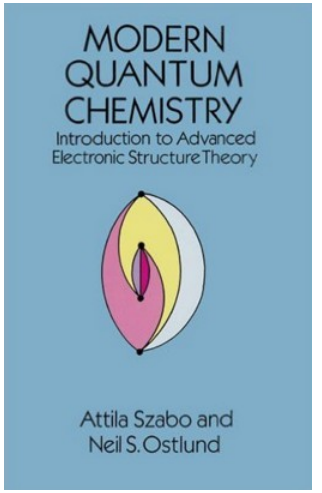


Figure 3.3 Comparison of the quality of the least-squares fit of a 1*s* Slater function ($\zeta = 1.0$) obtained at the STO-1G, STO-2G, and STO-3G levels.



- Coulomb integrals:

$$(\mu\,\nu|\frac{1}{\boldsymbol{r}}|\,\kappa\,\lambda) = \int d\boldsymbol{r}\, d\boldsymbol{r}'\, \phi_\mu(\boldsymbol{r})\,\phi_\nu(\boldsymbol{r})\,\frac{1}{|\boldsymbol{r}-\boldsymbol{r}'|}\,\phi_\kappa(\boldsymbol{r}')\,\phi_\lambda(\boldsymbol{r}')$$

=> from LIBINT library

Faleev *et al* Github (2016)

- XC functionals $\epsilon_{xc}(\rho(\boldsymbol{r}), \nabla\rho(\boldsymbol{r}))$ $\quad v_{xc}(\rho(\boldsymbol{r}), \nabla\rho(\boldsymbol{r}))$

=> from LIBXC library

Marques *et al* CPC (2012)

Analytic expression for Σ

$$G^{\sigma}_{0\,pq} = \sum_i \frac{\delta_{pq}\delta_{pi}}{\omega - \epsilon_{i\sigma} - \mathrm{i}\eta} + \sum_a \frac{\delta_{pq}\delta_{pa}}{\omega - \epsilon_{a\sigma} + \mathrm{i}\eta}$$

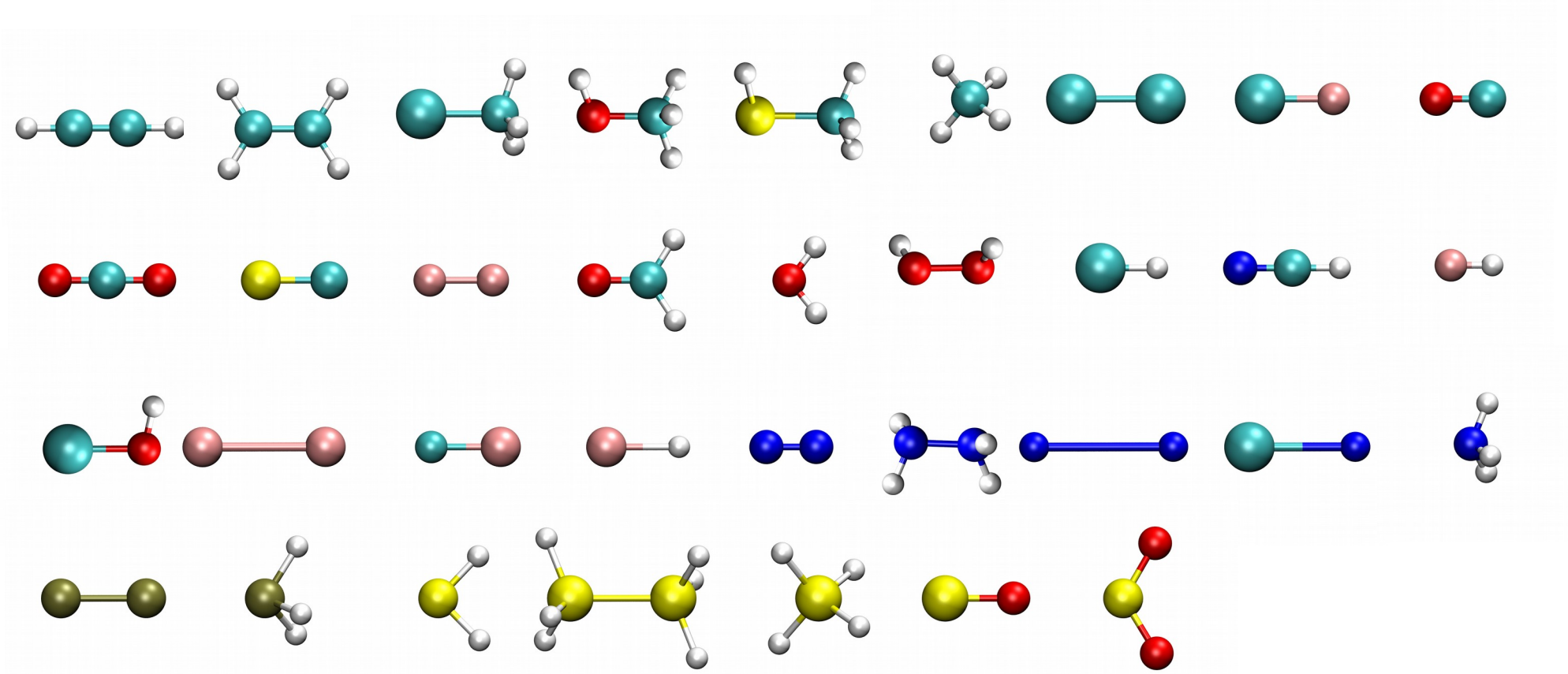
*

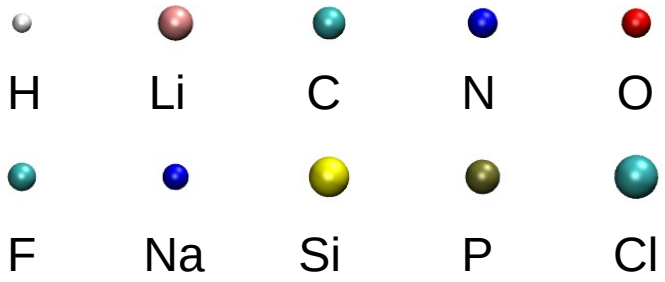
$$(v\chi^{\mathrm{RPA}}v)^{rt}_{pq}(\omega) = \sum_s w^s_{pq} w^s_{rt} \quad \left[\frac{1}{\omega - \Omega_s + i\eta} - \frac{1}{\omega + \Omega_s - i\eta}\right]$$

=

$$\Sigma^{\sigma}_{c\,pq}(\omega) = \sum_{is} \frac{w^s_{pi\sigma} w^s_{qi\sigma}}{\omega - \epsilon_{i\sigma} + \Omega_s - \mathrm{i}\eta} + \sum_{as} \frac{w^s_{pa\sigma} w^s_{qa\sigma}}{\omega - \epsilon_{a\sigma} - \Omega_s + \mathrm{i}\eta}$$

34 molecules benchmark: ionization potential





Reference IP's obtained within CCSD(T)

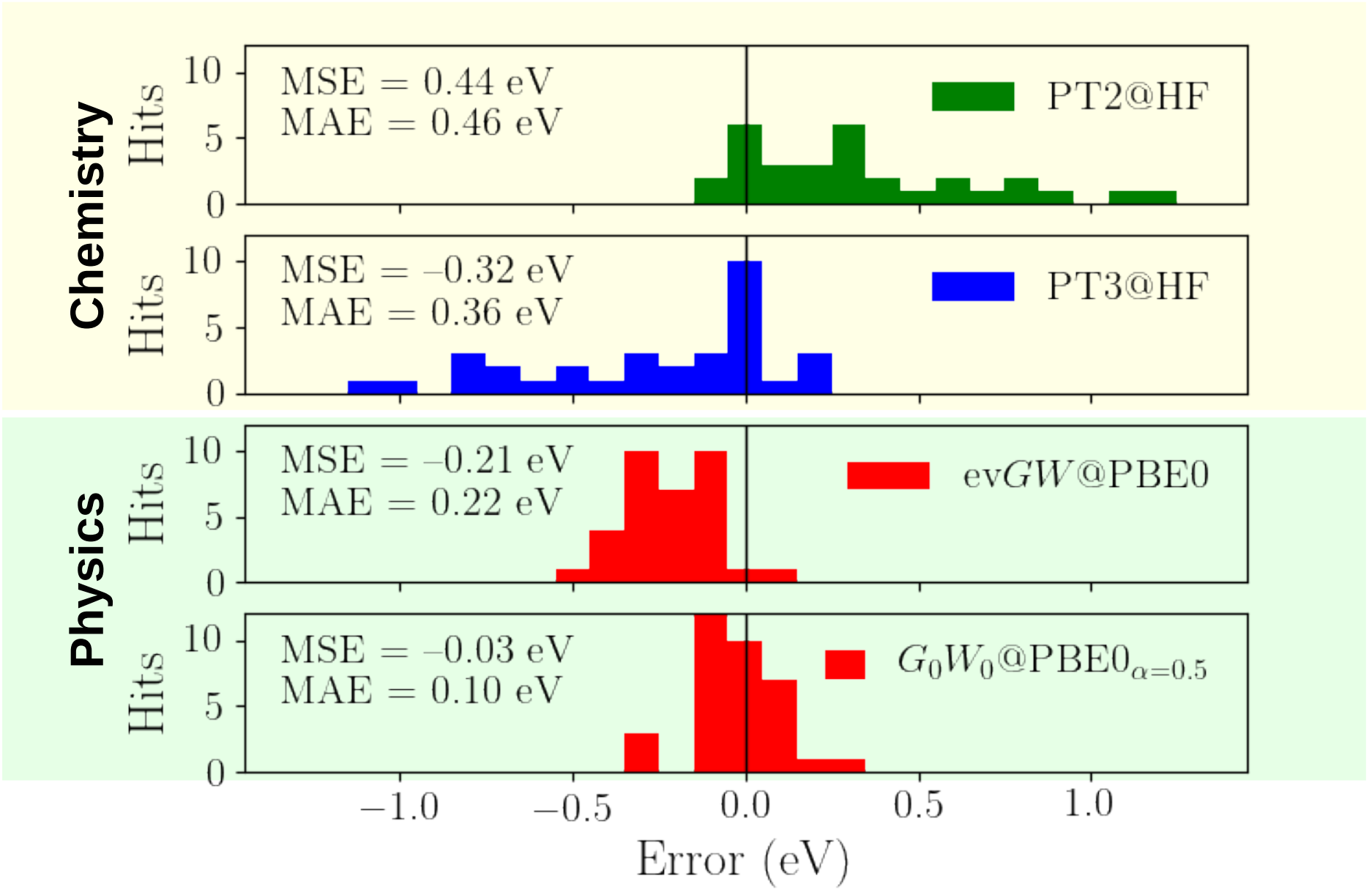
$$\mathrm{IP} = -\epsilon_{\mathrm{HOMO}}^{\mathrm{QP}} = E_{\mathrm{cation}}^{\mathrm{CCSD(T)}} - E_{\mathrm{molecule}}^{\mathrm{CCSD(T)}}$$

in a good basis set "cc-pVQZ"

F. Bruneval & MAL Marques, JCTC (2013)

Chemistry vs Physics: as of today

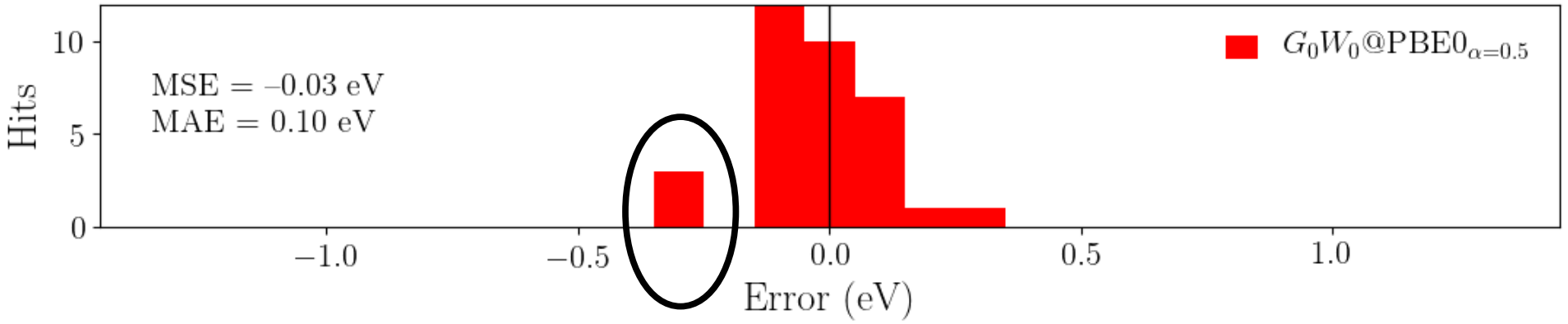
Today's best practices:



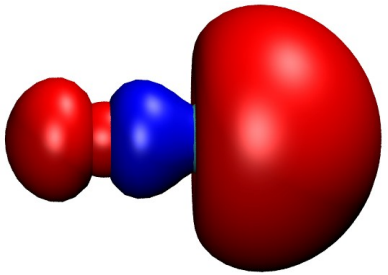
F. Bruneval, *GW* density matrix

Abidev, 2019

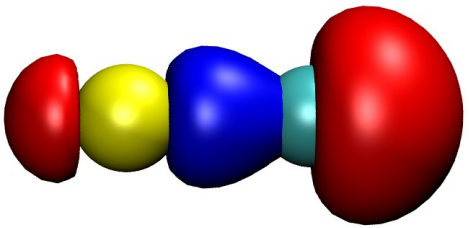
GW most noticeable failures



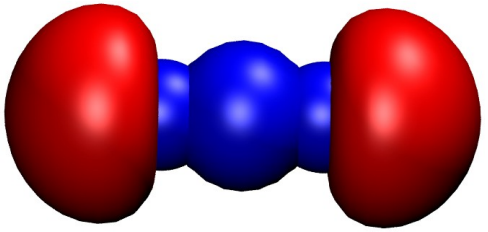
CO



CS



N_2

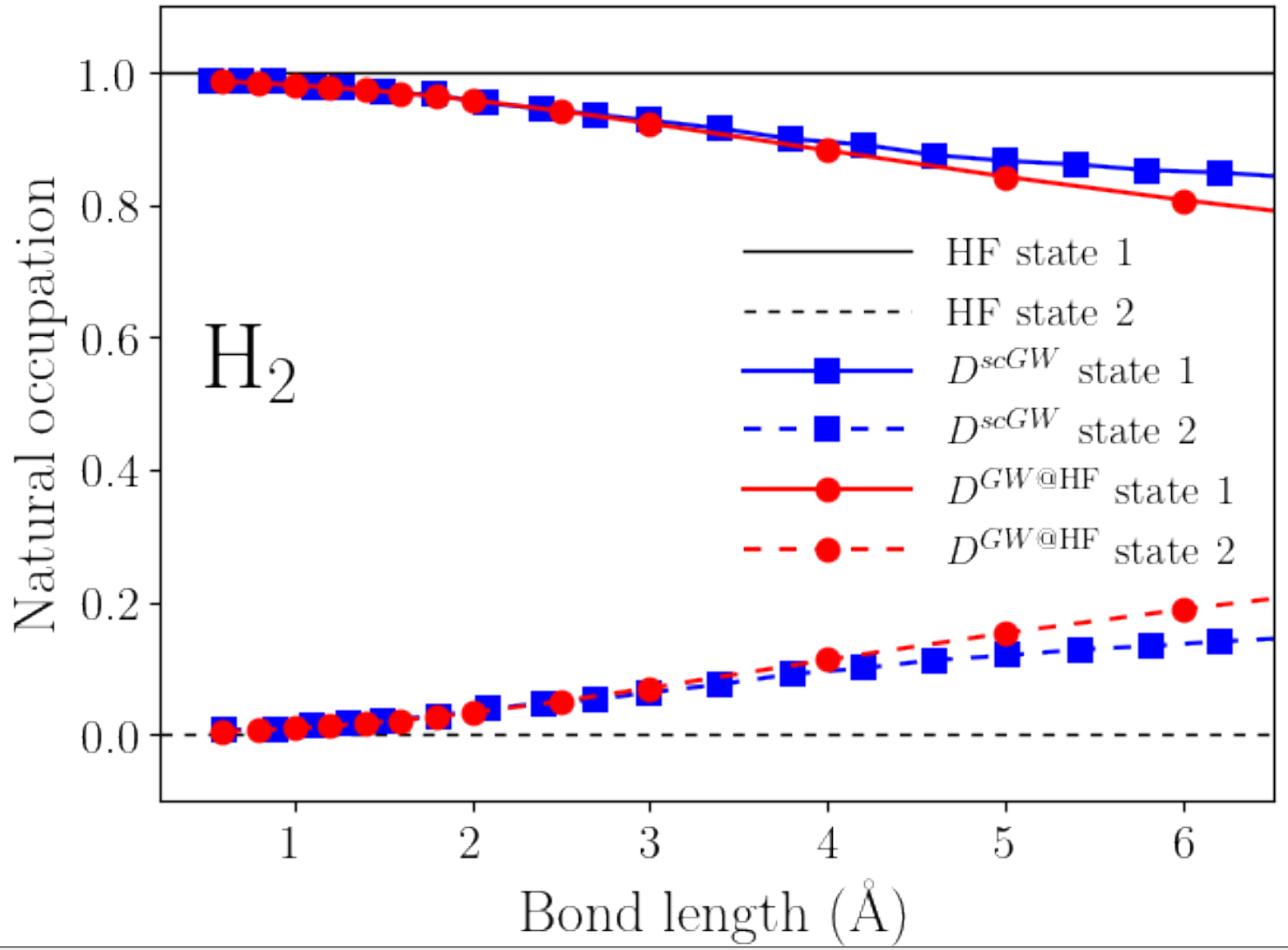


σ_p orbitals

Error: -0.33 eV -0.38 eV -0.42 eV

Natural occupation numbers

Eigenvalues of the density matrix



scGW: Hellgren, Caruso, Rinke, Rohr, Ren, Rubio, Scheffler, Phys. Rev. B (2015)

Total energies without self-consistency

GW correlation

$$E_c^{GW}[G] = \frac{1}{2}\int_{-\infty}^{+\infty}\frac{d\nu}{2\pi}\int d\mathbf{r}_1 d\mathbf{r}_2 \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}[\chi^1(\mathbf{r}_2,\mathbf{r}_1,\mathrm{i}\nu)-\chi^0(\mathbf{r}_2,\mathbf{r}_1,\mathrm{i}\nu)]$$

RPA correlation

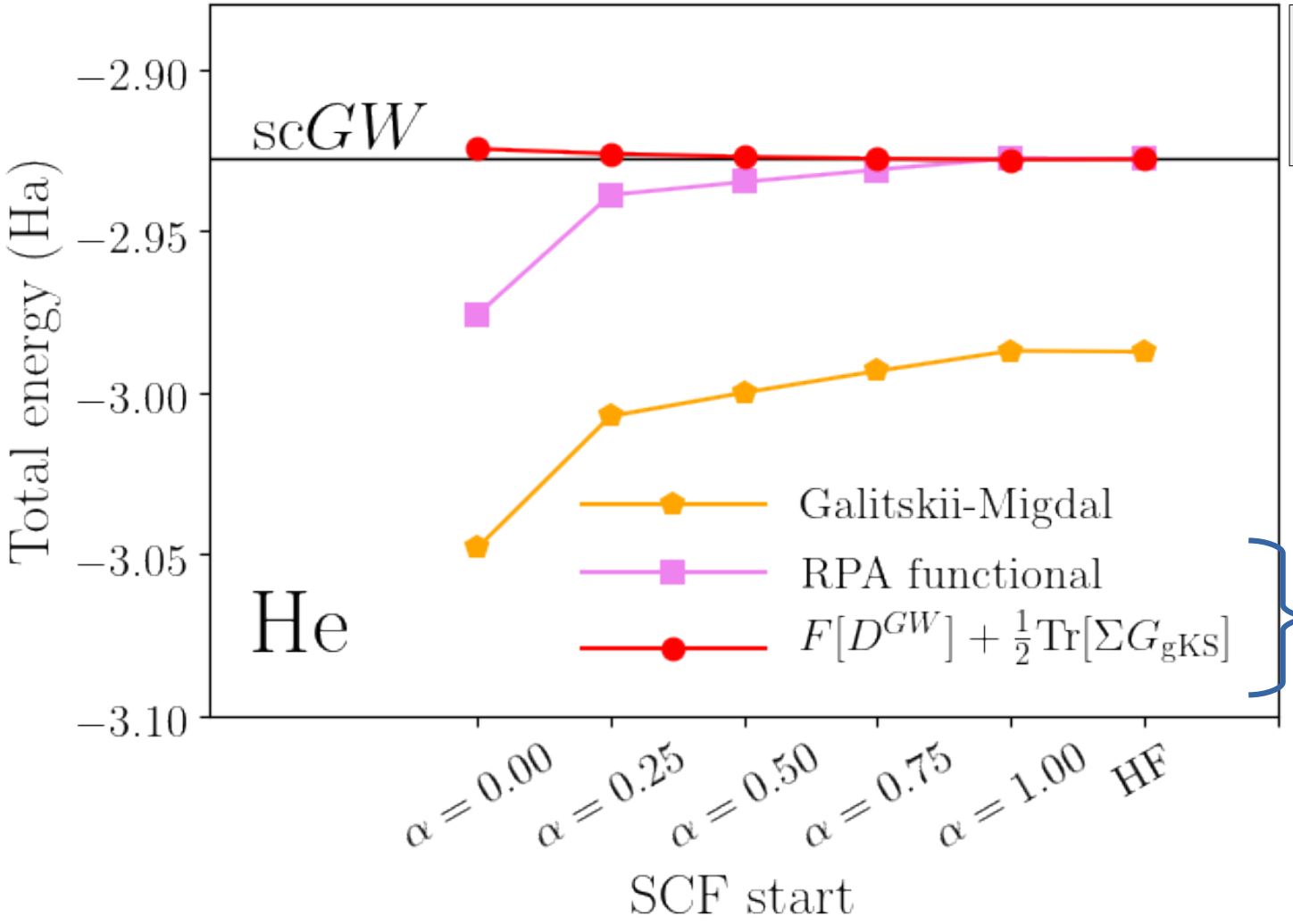
$$E_c^{\mathrm{RPA}}[G] = \frac{1}{2}\int_0^1 d\lambda\int_{-\infty}^{+\infty}\frac{d\nu}{2\pi}\int d\mathbf{r}_1 d\mathbf{r}_2 \frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}[\chi^\lambda(\mathbf{r}_2,\mathbf{r}_1,\mathrm{i}\nu)-\chi^0(\mathbf{r}_2,\mathbf{r}_1,\mathrm{i}\nu)]$$

Adiabatic connection captures the correlation part of the kinetic energy

	$F[\gamma^{gKS}]$	$F[\gamma^{GW}]$	E_c^{GW}	E_c^{RPA}
Galitskii-Migdal	■		■	
RPA	■			■
New proposal		■	■	

Stability of the energy functionals

Total energy evaluation starting from G^{gKS}



scGW: Stan et al., J. Chem. Phys. (2009)

Correlation part of Kinetic energy

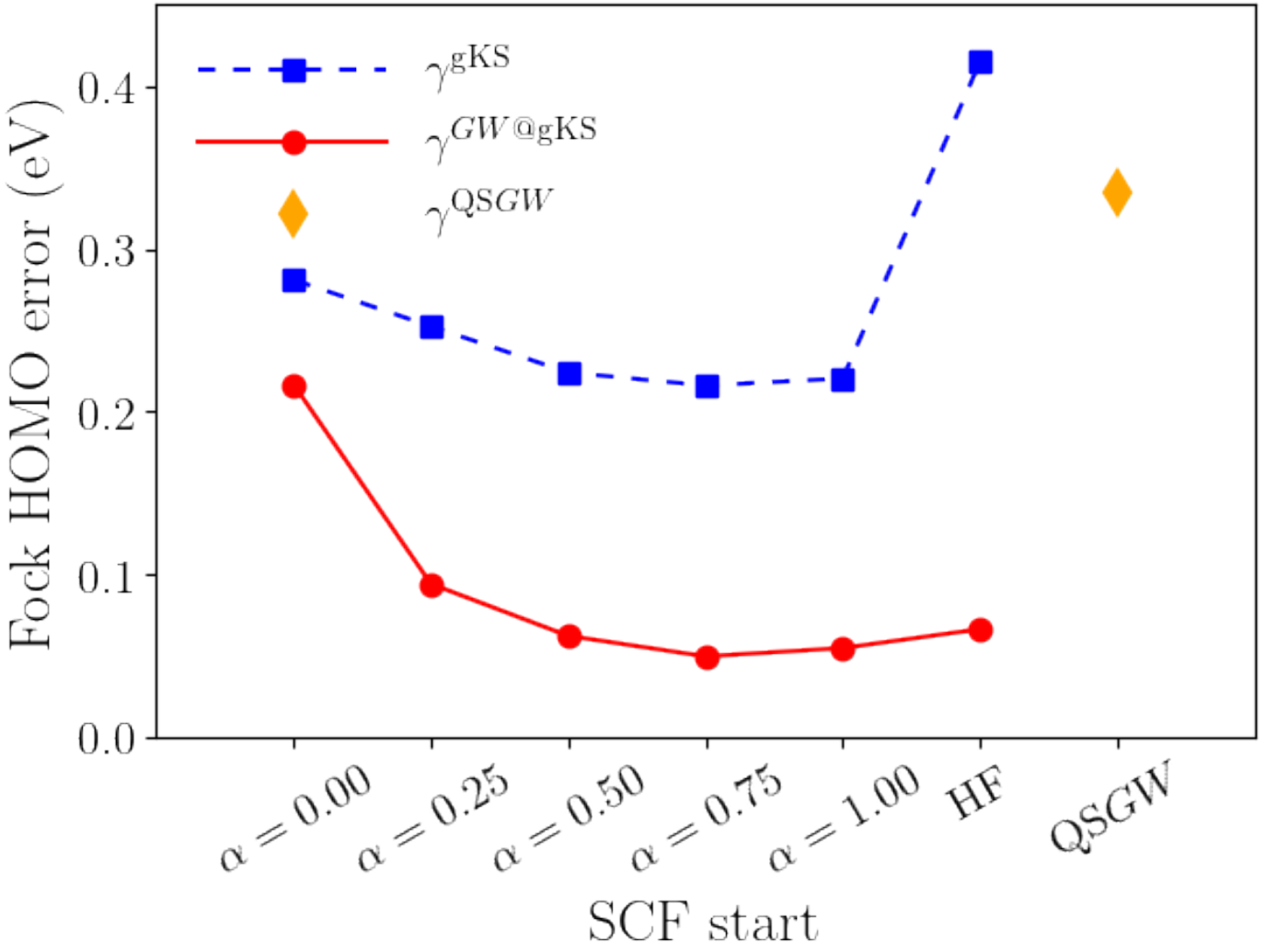
not included

included

Only one evaluation of the screened Coulomb interaction W!

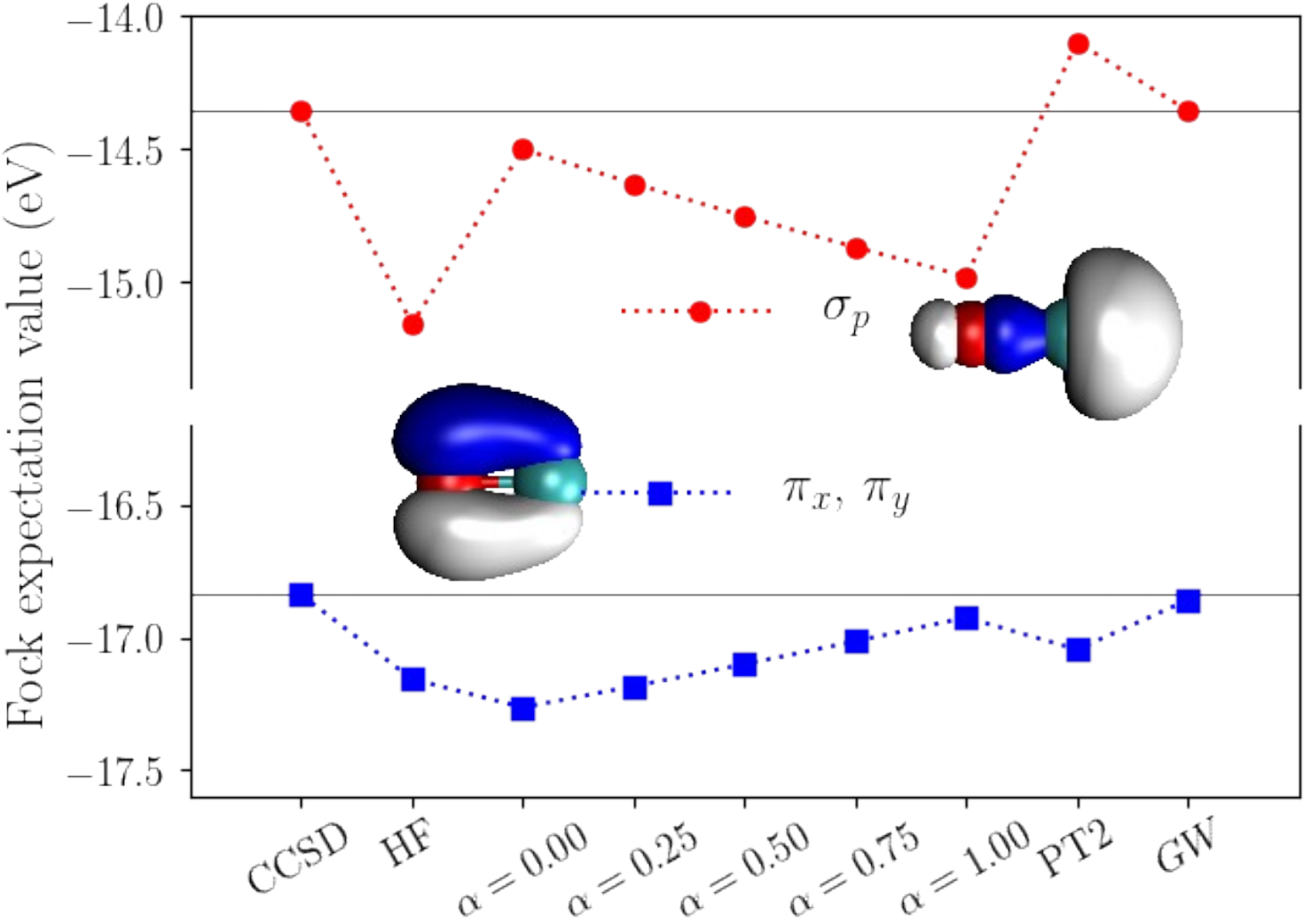
Entire Fock operator quality

$\langle \mathrm{HOMO} | F[\gamma] | \mathrm{HOMO} \rangle$



Density matrix effect on Fock operator

CO

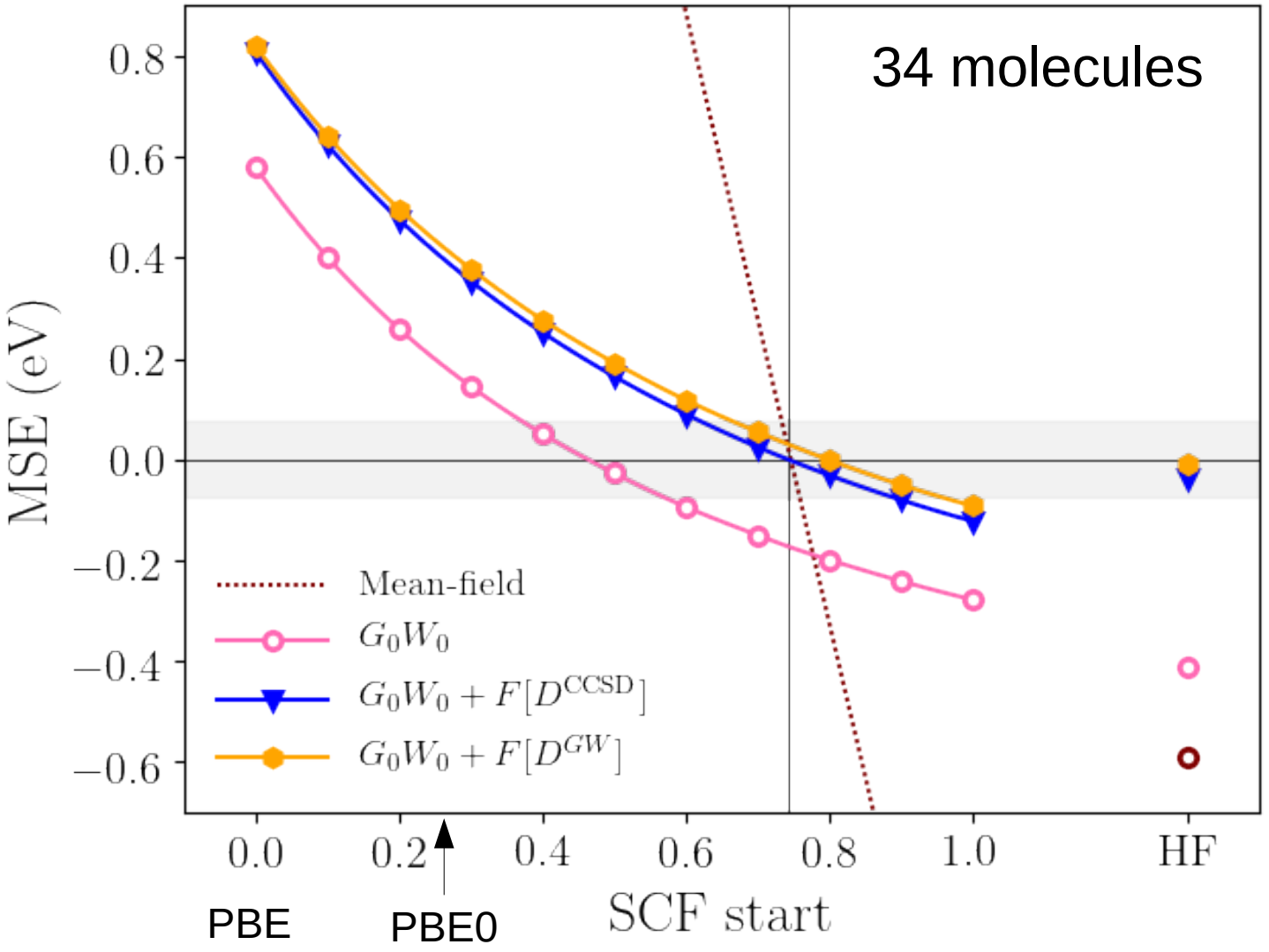


HOMO

HOMO-1

$$F_{pp} = \langle p| -\frac{1}{2}\nabla^2 + v_{ext} + v_H[D] + \Sigma_x[D]|p\rangle$$

IP from improved matrix density



- D^{GW} has a similar effect as D^{CCSD} (+0.2 eV)
- Best mean-field starting point corresponds to the best GW+$F[D^{GW}]$